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Ambiphilic ligands from the 1,4-benzenebis(amidine) framework

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The 1,4-benzenebis(*N*,*N*′-dialkylamidine) framework is used in the formation of polymeric species, and demonstrates the ability to combine both anionic amidinate and cationic amidinium moieties in the same species.

Amidinate anions, $[\mathrm{RC\{NR'\}_2}]^-$, constitute a family of ligands that are able to support a wide range of metal centres across the periodic table.[1] A recent development in this field has been the incorporation of greater than one amidine-based functional group in a single compound which, upon reaction with the appropriate metal substrates, results in the generation of multimetallic complexes. The nature of the linking unit determines the relative geometry of the amidinate moieties which, in turn, dictates the distance between and orientation of the coordinated metal centres. A number of examples have been presented in which the metals are remote from one another and linked by rigid spacer groups (Fig. 1A),[2] including earlier work in our group using a 1,4-benzenebis(amidinate) framework (Fig. 1B).[3] Using a more flexible group to join the amidinate functionalities (Figs. 1C and 1D) results in different types of coordination from the same class of ligand, where either chelation to,[4] or bridging between[5] metals has been observed.

Perhaps the most significant development in binucleating bis(amidinate) chemistry is the work of Hagadorn in which dibenzofuran and 9,9-dimethylxanthene are employed as bridging groups (Figs. 1F and 1E). Whilst monometallic species with chelating ligands have been observed,[6] the bimetallic systems are of more interest,[6,7] in which the framework ensures that the two metals centres are proximate to one another, with potential applications as bifunctional catalysts.[8]

In each of the cases cited above, the amidine moieties exist in either their anionic or neutral forms. No reports in which the ability of either of the groups to support a positive charge have been presented, despite the ready acceptance of a proton to form the amidinium cations, $[\mathrm{RC\{NHR'\}_2}]^+$. One of our interests in this area is the application of 1,4-benzenebis(amidine)s as building blocks in supramolecular chemistry, in which hydrogen-bonding is predicted to play an important role in the formation of certain extended structures. Consequently we consider both the amidinate and amidinium groups important, and report in this contribution a combination of both the positively and negatively charged forms *in the same molecule*.

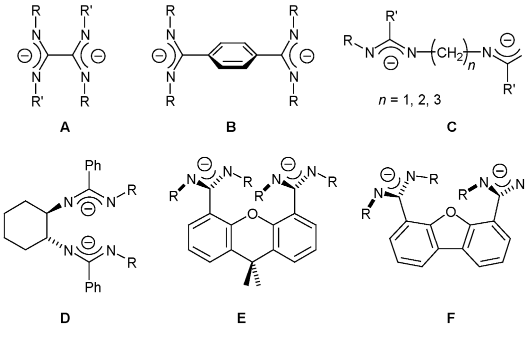
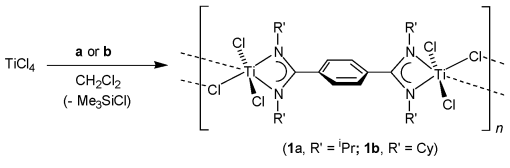


Fig. 1 Previously reported dianionic bis(amidinate) ligand frameworks.

Synthesis of $(\mathrm{1,4\text{-}C_6H_4[C\{NR'\}_2TiCl_3]_2})_n$ (**1a**, $\mathrm{R' = {}^iPr}$; **1b**, R′ = Cy) was achieved *via* addition of the corresponding *N*-silylated 1,4-benzenebis(amidines), $\mathrm{1,4\text{-}C_6H_4[C\{NR'\}\{N(SiMe_3)R'\}]_2}$ to $\mathrm{TiCl_4}$ at low temperature. An immediate colour change from yellow to red/purple indicated a rapid reaction, and an insoluble microcrystalline solid was deposited as the solution was stirred under ambient conditions. Elemental analysis and ^{1}H NMR data were consistent with clean formation of the bimetallic complex (**1a**), with sharp resonances at δ 3.48 and 1.42 (sept and d respectively) for the isopropyl substituents indicating a symmetrically bound amidinate unit. A small amount of an impurity (estimated at 3–5% by integration) was observed in the ^{1}H NMR spectrum for the cyclohexyl derivative however, revealed by the presence of a high field Si*Me₃* resonance and additional low intensity ligand resonances. In both cases, poor solubility hampered characterisation by ^{13}C NMR spectroscopy.

These data lead us to propose polymeric structures for **1a** and **1b** (Scheme 1), in which formation of extended chains is in agreement with the observed low solubility. Previously reported titanium mono(amidinate)[9] and mono(guanidinate)[10] trichlorides have been shown to consist of μ-dichloro-bridged dimers in the solid-state, and we therefore feel it reasonable to assume a similarly bridged linear arrangement is formed using the 1,4-benzenebis(amidinate) framework. Attempts at disrupting the chain through the addition of donor solvents were unsuccessful, suggesting a fairly robust link between the monomeric units.

In an attempt to purify **1b**, a solution of the crude product in $\mathrm{CH_2Cl_2}$ was layered with hexane, affording a small amount of a brown crystalline solid (**2**), believed to correspond to the impurity. The molecular structure is illustrated in Fig. 2, and selected bond lengths and angles are collected in Table 1. Compound **2** consists of the ionic species $[\mathrm{1,4\text{-}(C\{NHCy\}\{N(SiMe_3)Cy\})C_6H_4(C\{NCy\}_2)TiCl_3}][\mathrm{Ti_2Cl_9}]$, in which one of the amidines is present as the anionic amidinate, and the other exists as the cationic amidinium ion. The precise mechanism for the formation of this product is unclear, although the most likely scenario is the presence of HCl in the reaction, presumably a by-product of hydrolysis of $\mathrm{TiCl_4}$. The anionic amidi-



Scheme 1 Proposed structures of **1a** and **1b**. **a** = $\mathrm{1,4\text{-}C_6H_4[C\{N^iPr\}\{N(SiMe_3)^iPr\}]_2}$; **b** = $\mathrm{1,4\text{-}C_6H_4[C\{NCy\}\{N(SiMe_3)Cy\}]_2}$.

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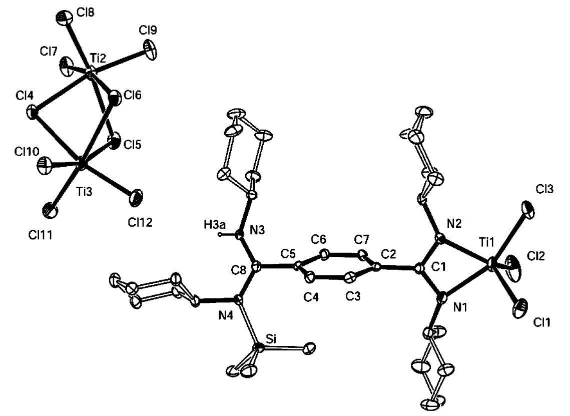

Fig. 2 Molecular structure of **2** (H-atoms except H3a omitted).

nate is bound through both nitrogen atoms to a titanium trichloride fragment, the first example of a five-coordinate mono(amidinate) titanium centre, in which no additional donor molecule stabilises the metal (closest intermolecular distances: Ti(1)···Cl(8) 4.53 Å; Cl(1)···Cl(8) 3.63 Å; Cl(2)···C(35) 3.72 Å; Cl(3)···Cl(2) 3.75 Å).[11] The resultant geometry at the titanium is approximately midway between trigonal-planar and square-based pyramidal, as defined by the τ parameter,[12] where the observed value of 0.58 for **2** lies between the predicted values of 1 for a perfect trigonal bipyramid (D_{3h}) and 0 for a perfect square-based pyramid (C_{4v}).

The bonding within the amidinate unit suggests an unequal distribution of electron density throughout the anionic unit. For example comparison of the C–N distances [1.355(5) Å and 1.308(5) Å] gives a Δ_{CN} value[13] of 0.047 Å, indicating significant asymmetry and a tendency towards a localised 'amide-imine' type of interaction. This also manifests itself in non-symmetric Ti–N distances [2.097(4) Å and 2.003(4) Å] where, as expected, the shorter metal–ligand interaction comes from the 'amido' nitrogen within the amidinate group (Fig. 3). We feel that this distortion is unlikely to be a consequence of the relative position of the nitrogen atoms (*e.g.* axial *vs.* equatorial) as a similar inequivalence has been observed in the chloride-bridged mono(amidinate),[9] and monomeric bis(amidinate)[14] complexes, in which the metal is distorted octahedral.

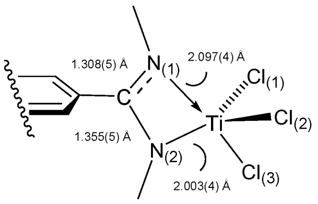

Fig. 3 Geometry around the titanium centre in **2**.

The protonated amidinium group of the ligand adopts an *E-syn* arrangement of *N*-alkyl substituents, also recently observed in the *N*,*N*′-diisopropyl-*N*-(trimethylsilyl)benzamidinium cation.[15] This contrasts with the arrangement in neutral a where the *E-anti* tautomer is observed in the solid-state. The carbon–nitrogen distances indicate a symmetrical distribution of the positive charge and no evidence of intermolecular hydrogen bonding is observed [shortest N*H*···Cl distance = 3.61 Å to Cl(7) of a neighbouring anion].

The anionic component of **2** consists of the $[Ti_2Cl_9]^-$ ion, first structurally characterised in 1971.[16] The titanium atoms are present in a face-shared bioctahedral arrangement, with average terminal and bridging metal chlorine distances of 2.214 Å and 2.492 Å, respectively.[16,17]

In order for there to be any significant conjugation between the π-systems of the amidinate and amidinium components across the bridging aryl ring, a small torsion angle (φ) must be present between these units and the C_6-plane. The incorporation of large alkyl groups in the nitrogen positions strongly disfavours this orientation on steric grounds, and the resultant values of φ [85.92(15)° and 64.09(17)°] and C_{ipso}–CN_2 distances [1.510(6) Å and 1.495(6) Å] for the amidinate and amidinium moieties, respectively, indicate isolated units. However, there is an implied influence that the amidinium unit exerts on the titanium centre, stabilising the monometallic centre with no μ-Cl ligands, which contrasts with previously observed 'Ti(amidinate)Cl$_3$' units and the proposed structure of **1**. Further studies are ongoing to develop rational syntheses of these zwitterionic systems and to assess further the relative effects that each component exerts on each other.

Experimental

Preparation of 1,4-$C_6H_4[C\{N^iPr\}_2TiCl_3]_2$ (1a)

A solution of **a** (0.50 g, 1.01 mmol) in dichloromethane (20 ml) was added dropwise at −78 °C to $TiCl_4$ (0.22 ml, 2.02 mmol) in

Table 1 Selected bond lengths (Å) and angles (°) for **2**

Ti(1)–N(1)	2.097(4)	Ti(1)–N(2)	2.003(4)
Ti(1)–Cl(1)	2.2003(16)	Ti(1)–Cl(2)	2.1940(17)
Ti(1)–Cl(3)	2.2497(18)	C(1)–N(1)	1.308(5)
C(1)–N(2)	1.355(5)	C(1)–C(2)	1.510(6)
C(8)–N(3)	1.309(6)	C(8)–N(4)	1.329(5)
C(8)–C(5)	1.495(6)	N(4)–Si	1.831(4)
$[Ti_2Cl_9]^-$			
Ti–Cl$_{terminal}$	*range*: 2.2018(16)–2.2277(15)		
Ti–Cl$_{bridging}$	*range*: 2.4633(15)–2.5103(16)		
N(1)–Ti(1)–N(2)	64.94(15)	N(1)–Ti(1)–Cl(1)	94.87(12)
N(1)-Ti(1)–Cl(2)	93.47(12)	N(1)–Ti(1)–Cl(3)	157.44(12)
N(2)–Ti(1)–Cl(1)	120.13(12)	N(2)–Ti(1)–Cl(2)	122.81(12)
N(2)–Ti(1)–Cl(3)	92.64(12)	Cl(1)–Ti(1)–Cl(2)	113.64(8)
Cl(1)–Ti(1)–Cl(3)	99.00(7)	Cl(2)–Ti(1)–Cl(3)	97.10(8)
N(1)–C(1)–N(2)	111.6(4)	N(1)–C(1)–C(2)	125.2(4)
N(2)–C(1)–C(2)	123.1(4)	N(3)–C(8)–N(4)	122.8(4)
N(3)–C(8)–C(5)	118.7(4)	N(4)–C(8)–C(5)	118.5(4)
Si–N(4)–C(8)	128.7(3)	Si–N(4)–C(27)	111.3(3)
C(8)–N(4)–C(27)	120.0(4)		
$[Ti_2Cl_9]$			
Ti(2)–Cl(4)–Ti(3)	86.77(5)	Ti(2)–Cl(5)–Ti(3)	86.25(5)
Ti(2)–Cl(6)–Ti(3)	86.01(5)		

dichloromethane (20 ml) resulting in the immediate formation of a red colour. The mixture was allowed to stir overnight, during which time a purple/red microcrystalline solid (**1a**) formed, which was isolated by filtration. Yield 0.53 g, 84%. Anal. calc. for $C_{20}H_{32}Cl_6N_4Ti_2$: C, 37.71; H, 5.06; N, 8.80%. Found: C, 37.95; H, 5.06; N, 8.67%. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.47 (s, 4H, C_6H_4), 3.44 (sept., 4H, C*H*Me$_2$), 1.33 (d, $^3J_{HH}$ = 7 Hz, CH*Me*$_2$). ^{13}C NMR (CD_2Cl_2, 298 K): δ 127.4 (*o*-C_6H_4), 54.2 (*C*HMe$_2$), 23.1 (CH*Me*$_2$). MS (EI, *m/z*): 483 $[M - TiCl_3]^+$, 447 $[M - TiCl_4]^+$, 330 $[M - Ti_2Cl_6]^+$.

Preparation of 1,4-$C_6H_4[C\{NCy\}_2TiCl_3]_2$ (1b)

A solution of **b** (0.50 g, 0.78 mmol) in dichloromethane (20 ml) was added dropwise at −78 °C to $TiCl_4$ (0.17 ml, 1.56 mmol) in dichloromethane (20 ml) resulting in the immediate formation of a red coloured solution. The mixture was allowed to warm to ambient temperature and stirred overnight, filtered and layered with hexane (30 ml) to give a microcrystalline solid **1b** and crystals of compound **2**. The latter were mechanically separated from the mixture and the X-ray diffraction study performed. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.55 (s, 4H, C_6*H*$_4$), 3.05 (m, 4H, NC*H*), 1.83–0.91 (m, 20H), 0.46, 0.45, 0.09.

X-Ray crystallography

A sample of the crystals of **2** were covered in oil and a suitable single crystal was selected under a microscope and mounted on a Kappa CCD area detector. The structures were refined using SHELXL-97.[18]

Crystallographic data for **2**: $C_{35}H_{58}Cl_{12}N_4SiTi_3$, M = 1132.04, T = 173(2) K, monoclinic, space group $P2_1/c$ (No. 14), a = 20.7206(6), b = 20.5047(5), c = 11.9981(3) Å, β = 93.101(1)°, U = 5090.2(2) Å^3, Z = 4, D_c = 1.48 Mg m^{-3}, μ(Mo-Kα) = 1.14 mm^{-1}, independent reflections = 7186 (R_{int} = 0.091), data/restraints/parameters = 7186/0/500, $R1$ [for 5086 reflections with $I > 2\sigma(I)$] = 0.051, $wR2$ (all data) = 0.100. CCDC reference number 244825. See http://www.rsc.org/suppdata/nj/b4/b409256b/ for crystallographic data in .cif or other electronic format.

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